

1

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PREPARATION OF URANIUM HEXACHLORIDE

Ross E. Van Dyke and Ernest Charles Evers, Providence, R. I., assignors to the United States of America as represented by the United States Atomic Energy Commission

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This invention relates to the production of uranium hexachloride. More particularly, it relates to the production of uranium hexachloride by treatment of uranium pentachloride, uranium tetrachloride, uranium trioxide or mixtures of two or more of these reactants with a mixture of liquid carbon tetrachloride and chlorine.

There is a present need for large quantities of uranium hexachloride. This recently discovered substance is an iridescent dark green crystalline material having a vapor pressure of approximately 1 to 3 mm. Hg at 100° C. It decomposes rapidly under ordinary atmospheric conditions, i. e., in the presence of moist air, but is stable in vacuum and dry air, nitrogen, helium, and the like, at ordinary room temperature. It is comparatively soluble in carbon tetrachloride.

It is therefore an object of the present invention to provide a process suitable for producing uranium hexachloride in good yield and of high purity by the reaction of uranium pentachloride, uranium tetrachloride, uranium trioxide or mixtures of two or more of these reactants with a mixture of liquid carbon tetrachloride and chlorine.

In accordance with the present invention, we have found that uranium hexachloride may be prepared by reacting a mixture of liquid carbon tetrachloride and chlorine with a material selected from the group consisting of uranium pentachloride, uranium tetrachloride, uranium trioxide, and mixtures of two or more of these reactants at an elevated temperature.

While uranium trioxide may be reacted directly with a mixture of liquid carbon tetrachloride and chlorine, it has been found that greatly increased yields result when uranium pentachloride and/or uranium tetrachloride are present in the reaction.

The following examples are given for purpose of illustrating the various specific embodiments of the invention. It will be understood that these examples are given by way of illustration and not by way of limitation. All parts are given by weight unless otherwise specified. The pressure value as given in the examples is in pounds per square inch gauge unless otherwise specified.

Example I.—Conversion of UCl₅ to UCl₆

A charge consisting of 1000 g. UCl₅, 1600 g. CCl₄ and 160 g. Cl₂ was heated at 115° C. in a stainless steel autoclave and, after the heating period specified in Table 1, below, the reactor was cooled to approximately 50° C. and samples of the liquid phase were withdrawn for analysis.

TABLE 1

[Rate of formation of UCl₆ as a function of heating time at 115° C. Solvent contains 10% Cl₂.]

Exp. No.	Heating Time, Hours	g. UCl ₆ /100 g. Solution
A	2	9.4
	4	11.3
	6	10.4
	2*	8.0
B	4	11.3
	6	10.6

2

In the above two experiments, it may be seen that reaction, as measured by the concentration of UCl₆ in the solvent phase, was virtually completed in two hours, the production rate for a two-hour reaction being approximately 40-45 g./kg. CCl₄/hour.

Example II.—Conversion of UO₃ to UCl₆ with UCl₅ added as promoter

Experiments showing the influence of temperature and Cl₂ concentration on conversion of UO₃ to UCl₆ in the presence of UCl₅ are presented in Table 2. In each experiment, the charge consisted of 213 g. UO₃, 620 g. UCl₅ and 3200 g. CCl₄. This quantity of oxide would give, theoretically, a 9% solution on complete conversion to UCl₆; the mole ratio of UCl₅/UO₃ was 2:1. The reactions were carried out for three hours at the temperatures indicated. The reactor was cooled to approximately 50° C. and samples of the liquid phase were withdrawn for analysis. Included in the table is the maximum pressure recorded during each experiment.

TABLE 2

[Conversion of UO₃ to UCl₆ and the yield of UCl₆ as a function of Cl₂ concentration for constant charge. Three hours' heating at reaction temperatures ranging between 115° and 150° C.]

Exp. No.	Reaction Temp., ° C.	Percent Cl ₂	Gauge Pressure, lb./in. ²	Percent Conversion of UO ₃		g. UCl ₆ per 100 g. CCl ₄
				UCl ₅	UCl ₆	
A	115	19.1	202	144	¹ -44	15.6
B	115	13.0	151	119	-19	12.7
C	125	11.7	164	113	-13	12.0
D	150	7.1	194	83	17	8.9
E	115	5.5	98	78	22	8.2

¹ Negative sign indicates conversion of UCl₅ to UCl₆.

On holding the charge constant, it may be seen that the conversion to UCl₆ decreases with decreasing Cl₂ concentration under the conditions employed in reaction.

The reaction may be conducted in an autoclave, or other essentially gas-tight closed vessel capable of withstanding the pressure developed during the operation. This autoclave or reactor may be constructed of stainless steel, glass-lined iron or steel, or other suitable resistant material, and should be provided with an agitator, inlets for introduction of the reactants, and outlet in the bottom of the reactor for removal of the reaction products, and an outlet or outlets in an upper portion of the reactor for removing or venting vapors and gases. Ordinarily, carbon tetrachloride is used in sufficient excess that this recovery operation is not used. The reactor and condenser may be suitably jacketed and provided with the usual means for circulating heat exchange fluid through the jackets. Safety valves, pressure and temperature indicating and/or recording devices may be provided if desired.

The uranium compounds which may be chlorinated to uranium hexachloride by this process are uranium trioxide, uranium tetrachloride, uranium pentachloride, and mixtures thereof. If uranium trioxide alone is used, it has been found that higher yields of uranium hexachloride may be obtained by adding additional chlorine to the reaction from time to time as the reaction progresses.

The process is preferably conducted in the presence of a substantial excess of carbon tetrachloride. For best results the amounts of the components of the charge to the autoclave are adjusted so that the solution is saturated with UCl₅ at all times. Preferably, where uranium trioxide is a reactant the ratio of this oxide to carbon tetrachloride should be adjusted so that the